# THERMAL RUNAWAY IN LARGE ANFO CHARGES

Douglas Olson and Marvin Banks
Research Center for Energetic Materials
New Mexico Tech, Socorro, NM 87801

## SUMMARY

The purpose of this work was to determine the potential thermal hazards from self-heating of large ANFO charges. To accomplish this objective, the thermal stability of ANFO was determined from measurements of the critical temperature (i.e., the minimum temperature at which thermal runaway occurs) at three sample sizes: 40 mg, 25 g, and 25 kg. The effective thermal conductivity of solid ANFO at density 0.85 g/cm$^3$ was measured as 0.11 W/(m K) using a specific heat value of 1.5 J/(g K). The cook-off data were used to determine the decomposition rate coefficient from 168 to 297$^o$C—a range covering over five decades in reaction rate. The resulting Arrhenius rate constant expression was k = 5.3 x 10$^{15}$ exp(-46.04/RT) s$^{-1}$, with the activation energy in kcal/mol units.

The experimentally-determined ANFO parameters were incorporated into two models to investigate the potential for thermal runaway of ANFO charges of various sizes and for various initial conditions. If the initial temperature of ANFO loaded into a large container [for example, a hemisphere of 2,400 tons (20 meters (70 feet) in diameter)] is near ambient, the models indicate that no credible external heating is likely to bring the material to a homogeneous runaway condition.

## INTRODUCTION

The explosive material used in the largest quantity per year in the world is ammonium nitrate (AN) mixed with a near stoichiometric amount (about 6 wt%) of hydrocarbon fuel oil (FO). Millions of pounds of this mixture, denoted ANFO, are produced each year and used for about 80 percent of all commercial blasting operations. The US consumption of ammonium nitrate based explosives was 4.0 billion pounds in 1991. Large quantities of ANFO are therefore handled in manufacturing and transportation operations. The thermal stability and initiation insensitivity of ANFO are very high, making ANFO very safe to handle and store, especially when compared with previously used commercial explosives such as dynamite.

The purpose of this study was to quantify the thermal hazards inherent in using large charges of ANFO. For example, over the past several years ANFO charges from about 2400 to 4800 tons (2.2 - 4.4 x 10$^6$ kg) have been used to simulate the environments caused by nuclear weapons. In hemispherical shapes, these weights represent quantities of ANFO with diameters of 2140 and 2700 cm (70 and 88 feet). The main question addressed in this work was whether it is possible for ANFO charges of this size to self-heat as a result of chemical decomposition heat which cannot be conducted away as fast as it is generated.

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# BACKGROUND

## Thermal Decomposition Kinetics From Cook-off Data

Thermal methods of measuring reaction rates rely on the heat produced (or absorbed) by a system as a measure of the amount of reaction.  We have utilized thermal runaway (isothermal cook-off) tests on ANFO to determine critical temperatures (i.e., minimum temperatures for runaway self-heating) from which we have derived steady-state global reaction rates.  Since different sample sizes yield different critical temperatures (i.e., different rates of reaction), we have been able to determine the global rate constant parameters for ANFO decomposition over a range of over five decades.

Thermal runaway from exothermic reactions is possible for many chemicals and energetic materials.  This happens when the rate of heat generation from chemical decomposition exceeds the rate of heat loss from the material.  At the critical temperature, these two rates are equal.  Quantitatively describing the rate of heat loss by conduction from simple sample configurations is a relatively straightforward problem; once the problem is solved, the rate of heat generation can be determined.  Since the rate of heat generation is the product of the reaction rate and the heat of reaction, the reaction rate can be determined if the heat of reaction is known.  Cook-off tests on samples of approximately 25 kg or so yield rate constant determinations in the $10^{-8}\,s^{-1}$ range, whereas tests on smaller samples yield rate data at much higher values, about $10^{-6}$ and $10^{-2}\,s^{-1}$ for 1 kg and 40 mg samples, respectively.  The corresponding rate constant at the critical temperature for approximately 2,000 tons would be in the $10^{-11}\,s^{-1}$ range.

## Thermal Explosion Model

The theory of thermal ignition has been treated by many workers, including Zeldovitch, et al.[1] (1939), Frank-Kamenetskii[2] (1939), Gray and Lee[3] (1968), Zinn and Mader[4] (1960), Zinn and Rogers[5] (1962), and many others.  For solid explosives, consideration can be confined to conductive heat losses [i.e., the well-known Frank-Kamenetskii (F-K) model].  The assumptions and limitations of this model have been discussed by the authors listed above.  In the case of symmetric configurations, the F-K formula gives the critical temperature (Tc, K) as

# EQUATION

$$Tc = \cfrac{Ea/R}{\ln\left[\cfrac{r^2 \rho\, Q\, A\, Ea}{Tc^2 \lambda\, Sh\, R}\right]},$$

where  
    $Tc$ = Critical temperature, K  
    $Ea$ = Activation energy, cal/mol  
    $A$ = Preexponential factor, $s^{-1}$  
    $R$ = Gas constant, 1.987 cal/K/mol  
    $r$ = Radius or half-thickness, cm  
    $\rho$ = Density, $g/cm^3$  
    $Q$ = Heat of decomposition reaction, cal/g  
    $\lambda$ = Thermal conductivity, cal/cm/s/K  
    $Sh$ = Shape factor, 3.32 for sphere, 2.0 for infinite cylinder, 0.88 for slab, 2.5 for cylinder with length approximately equal to diameter

The main unknowns in the F-K analysis are the thermal conductivity, the heat of reaction, and the Arrhenius rate constant parameters, A and Ea, which give the rate constant (k) value at any temperature as $k = A \exp(-Ea/RT)$. The density, radius, and shape factor are usually known. If all these parameters are known, accurate predictions of critical temperatures can often be made (when the situation fits the assumptions of the F-K model).

Conversely, if the critical temperature is experimentally measured and the thermal conductivity is known, combinations of A and Ea can be determined which satisfy the F-K formula. It is found that if Ea is estimated and the A-factor is determined, the resulting value of k is only slightly dependent upon the value of Ea used. Thus we can determine a value for k at the temperature Tc by measuring the critical temperature of an explosive in a given sample size and shape. Other rate constant values at different temperatures can be determined by measuring critical temperatures for other sample sizes. A fit to these k(Tc) data points vs. 1/T yields a global rate coefficient which will describe cook-off behavior for this explosive over a wide range of conditions.

## General Properties of AN and ANFO[8]
Crystalline ammonium nitrate absorbs water from the air and forms hard cakes which makes it difficult to handle (e.g., to spread as a fertilizer). These handling difficulties led to the manufacture of prilled AN (i.e., small—approximately 2 mm diameter—balls of AN created by spraying AN solution in a drying tower). After about 1945, the residual moisture content of the prills was allowed to increase, producing a higher porosity AN denoted as fuel-grade ammonium nitrate (FGAN). The previously used low porosity AN was called explosive-grade ammonium nitrate. The available porosity in FGAN of about 0.07 $cm^3/g$ is almost exactly the amount needed to absorb the quantity of oil to yield an oxygen balanced (stoichiometrically balanced to $CO_2$ and $H_2O$ reaction products) ANFO product. The AN

prills also contain unavailable porosity (i.e., not available to absorb oil) which is also important in giving the ANFO a low final density and in sensitizing it to shock initiation.

AN has several solid state phases over the temperature range of interest. This complicates its use in applications where expansion may cause difficulties. Of special interest are the expansions and heats of transition that occur at the IV to III transition at 32.3$^{\circ}$C, the III to II transition at 84.2$^{\circ}$C, and the II to I transition at 125.2$^{\circ}$C before melting at about 169$^{\circ}$C.

The explosive characteristics of FGAN became widely recognized after the explosion of a shipload of over 3,000 tons at Texas City in 1947. The specific product that exploded was FGAN coated with about 1 percent wax for anti-caking purposes. (Actually the "wax" was a mixture of paraffin, rosin, and petrolatum.) However, this mixture is more sensitive than either pure AN or the oxygen balanced mixture with 5.5 percent wax. The explosion was caused by several factors: the relatively high sensitivity of the wax-coated FGAN; the large charge size; the high initial temperature, about 32$^{\circ}$C; and the paper bags in which the material was shipped. It is likely that the paper-AN combination exhibited a lower thermal stability than the FGAN itself and it self-heated, possibly starting the fires that ultimately lead to detonation of the whole shipload of FGAN. Following the Texas City incident, the anti-caking wax coating was replaced by a coating of kieselguhr.

**Decomposition Kinetics of AN/Fuel Mixtures**
Although the literature on the thermal stability of AN is extensive, few studies have been performed on ANFO. Hainer[6] studied the thermal decomposition of AN and 3 percent wax-coated fertilizer grade AN (FGAN) using weight loss and $N_2O$ evolution measurements over the temperature range 220-290$^{\circ}$C for AN and 70-230$^{\circ}$C for FGAN. At the lower temperatures, samples as large as 100 pounds were used for gas evolution measurements, resulting in rate constant determinations as small as 3 x $10^{-9}$ s$^{-1}$ at 132$^{\circ}$C for AN and 2-10 x $10^{-12}$ s$^{-1}$ at 70$^{\circ}$C for FGAN. No other measurements at these low reaction rates are available for either material. Hainer's kinetic results (Ea in kcal/mol units) for FGAN are k = 3.7 x $10^{10}$ exp(-34.8/RT) s$^{-1}$. Hainer concluded that the reaction rates of AN and FGAN were similar at high temperatures (>200$^{\circ}$C), but that of FGAN was much larger at low temperatures (by about 100 times at 100$^{\circ}$C).

Oxley, Kaushik, and Gilson[7] studied AN, emulsion, and AN mixed with 5 wt% mineral oil (denoted ANMO to differentiate it from commercial ANFO) by isothermally decomposing the test material sealed in glass tubes and by using DSC techniques. ANMO reacted slightly faster than neat AN at temperatures higher than about 270$^{\circ}$C. However, at lower temperatures, the ANMO reaction was faster than AN only for the initial part (40 percent at 270$^{\circ}$C, decreasing to 14 percent at 230$^{\circ}$C) of the decomposition. Kinetic parameters were determined for both the more rapid initial (denoted "early") and the slower final (denoted "late") portions of the total reaction. The early kinetics of ANMO decomposition were characterized over the temperature range 230-370$^{\circ}$C by k = 2.4 x $10^{11}$ exp(-35.2/RT) s$^{-1}$ .

The kinetic data for the two studies of AN/fuel are plotted in Arrhenius form in Figure 1 for comparison. The activation energies of the two expressions are similar, with the two lines

offset from each other by about a decade.

**Decomposition of AN**

Extensive literature exists on AN decomposition, including information on kinetics, mechanisms, catalyst, and product composition. King and Bauer[8] at Queens University, Ontario, reviewed the literature on AN and published a series of twelve reports. Number four of this series covers thermal decomposition mechanisms and kinetics up to 1974. Report number one covers accidents with AN and number nine covers the deflagration to detonation transition in molten AN.

Robertson[9] studied isothermal AN decomposition by pressure measurements over the temperature range 243-361°C. This work extended to higher temperatures than are typical. The results were fit to the Arrhenius expression $k = 6.3 \times 10^{13} \exp(-40.5/RT)$ s$^{-1}$, with an estimated uncertainty of ±2.5 kcal/mol in the activation energy. These rate constant results are higher than reported in most other work done in this temperature range.

Hainer's kinetic results for AN (220-290°C) from the same study[6] as discussed above were $k = 8.4 \times 10^{18} \exp(-55.6/RT)$ s$^{-1}$. It should be noted that these data for AN did not cover as extensive a temperature range as for the FGAN data.

Cook and Abegg[10] studied AN decomposition using real time weight loss measurements over the temperature range 218-267°C. First order behavior was observed in all experiments, with no autocatalysis. Their rate constant was $k = 1.9 \times 10^{12} \exp(-38.3/RT)$ s$^{-1}$. Cook and Abegg's expression was corrected for AN vaporization by King and Bauer[8] to give $k = 4.9 \times 10^{11} \exp(-37.0/RT)$ s$^{-1}$.

Keenan and Dimitriades[11] used a gas evolution method to study the decomposition of AN from 230-265°C. Their results gave $k = 3.0 \times 10^{16} \exp(-49.5/RT)$ s$^{-1}$.

Rosser, Inami, and Wise[12] studied AN decomposition from 225-275°C using $N_2O$ evolution rates in a flow system. By seeding the inlet gas flow, they showed clearly that $NH_3$ and $H_2O$ inhibit AN decomposition, and $HNO_3$ promotes AN decomposition; thus the overall rate of decomposition depends on the gas composition in contact with the AN. Their nominal rate constant was $k = 1.8 \times 10^{13} \exp(-41.0/RT)$ s$^{-1}$.

Brower, Oxley, and Tewari[13] calculated rate constants for AN decomposition in sealed glass tubes from total gas evolution and nitrogen fraction measurements over the temperature range 200-380°C. Their data were fit to separate high and low temperature expressions $k = 8.5 \times 10^{14} \exp(-46.3/RT)$ s$^{-1}$ (high temperature), and $k = 1.3 \times 10^8 \exp(-28.2/RT)$ s$^{-1}$ (low temperature).

The kinetic data for AN are plotted in Arrhenius form in Figure 2 for comparison. Although all of these rate constant expressions were derived from data which agree fairly well (within a factor of ten) in the temperature regions of overlap, they were almost all measured at relatively high temperatures. If these expressions are extrapolated to the lower temperatures,

which are of interest for storage stability considerations for large quantities of AN or ANFO, the disagreement is much larger.

## EXPERIMENTAL

### Cook-off Tests

The critical temperatures, Tc, were determined for three different sample sizes of ANFO.

### Henkin-McGill Tests.

The Henkin-McGill test[14] is the smallest thermal runaway test. It has the advantage of being small enough, using samples of less than 0.1 g, to be run in the laboratory environment using an apparatus similar to those described by Rogers.[15]

Ground ANFO samples were sealed inside standard aluminum blasting-cap shells using a hand-operated hydraulic press and specially made hollow aluminum plugs. A two-step pressing procedure was used to compress the sample and then to expand the wall of the plug to create a seal with the shell. A micrometer was used to measure the thickness of each disc. The sample was lowered into the hot molten Wood's metal bath in a remote operation using a compressed air-driven piston/cylinder. The time-to-explosion was measured using a stopwatch from the initial time when the sample was immersed in the bath to the time, if any, at which the sample holder ruptured. The timing uncertainty was estimated to be about plus or minus one second. To find the critical temperature, the time-to-explosion tests were repeated at various temperatures until the minimum temperature was found at which thermal runaway and shell rupture occurred.

### SSCB Tests.

Pakulak and Cragin[16] developed a small cook-off test, called the super small cook-off bomb (SSCB) test, using a 5/8 inch (1.6 cm) i.d. tube with witness plates bolted directly to the open ends of the tube to contain the explosive. In the work reported here, a modified SSCB apparatus, based loosely on the Navy test, was used. Thick-walled aluminum tubing with 2.5 cm o.d. and 1.6 cm i.d. was threaded and sealed using stainless steel pipe caps on each end. A thermocouple was installed through the bottom end cap to measure the axial sample temperature. The assembled tube containing the explosive was heated by contact with a split 4 inch (10 cm) diameter brass platen containing four embedded 250 Watt electric cartridge heaters. Heating time from ambient was about 10 minutes. The tests reported here were run vented to the atmosphere.

The thermocouple located inside the test vessel and the two thermocouples located in the platen were connected to a personal computer using an Omega Engineering, Inc. White Box interface card and software. The software was programmed to record the temperatures at one-minute intervals. The data acquisition board was checked prior to each test using a precision voltage source thermocouple calibrator. The channels typically agreed within $\pm 0.1 °C$. The desired platen temperature was also programmed into the Omega software which then controlled a solid-state relay connected to the electric heaters. ASCII data files were imported into a Quattro Pro spreadsheet for data analysis and plotting.

**1-Liter Cook-off Tests**
Charges of about 0.8 kg of ANFO were tested using glass round-bottomed flasks as charge containers with three thermocouples located at the sample center, mid-radius, and wall. The sample was heated using a stirred hot oil bath using Dow Corning 200 heat transfer fluid. Another thermocouple was inserted into the oil bath to monitor its temperature. A stirrer was used to obtain uniform oil temperature. The same data acquisition and data reduction methods used for the SSCB tests were used here.

**32-Liter Cook-off Tests**
Larger quantities of ANFO were used to perform thermal runaway tests on the material at temperatures below the melting point (165-169ºC). To minimize fragments should the charge detonate, a test vessel was fabricated based on a 32-liter, heavy-walled glass battery jar (41 cm diameter, 31 cm deep) with a lightweight aluminum lid. Silicone rubber-insulated, flexible electric heating bands were used on the top, bottom, and sides of the vessel for heating. Insulating blanket material was also wrapped around, over, and under the vessel.

Three thermocouples were located in the charge and connected to voltage-to-current modules (Omega Engineering, OM3 modules) using eight-pair K-type thermocouple wire cable to transmit the signals over approximately 210 meters (600 feet) of shielded multi-pair cable to the instrumentation bunker. These tests utilized the same type of computer and interface board that were used for recording the data and controlling the heaters for the SSCB and 1-liter tests. The analog-to-digital board was reprogrammed from direct processing of thermocouple voltage inputs to processing of 20 milliampere current loop signals. Remote control software (Close-Up) and high-speed modems were installed on the computer used to control the test temperature and record the data located at the cook-off site as well as on computers used for remote monitoring of the test progress. The absolute calibration of the thermocouples and voltage-to-current modules were checked using a voltage source calibrator just prior to beginning the test. Slight linear offsets were applied to the various thermocouple signals in the data acquisition program to bring them into agreement within ±0.5ºC.

A plywood box was placed over the whole apparatus to provide protection from weather. These tests were performed at a remote fast/slow cook-off site which is rated for large explosive charges and has continuous video surveillance for security.

**Test Material**
Commercial ANFO obtained from ICI Explosives in Albuquerque, NM was used for all tests. The ANFO was used as received except for grinding it for Henkin-McGill tests (where the prills were too large).

**RESULTS**

**Densities and Melting Point**
The density of the ANFO was measured four times using a cup of known volume and a precision balance. The results were an ANFO density of 0.85±0.01 g/cm$^3$. The average

density of the Henkin-McGill samples which were pressed into the shells for testing was measured in place as about 1.65 g/cm$^3$.

The melting temperature of this ANFO was measured using about 2 grams of material inside a test tube heated by an oil bath.  Some melting (wetting) was observed at 160ºC, but melting was not complete until about 170ºC.  Melting tests were also performed using a Mettler hot stage with microscopic observation.  No melting was observed below 167.6ºC, with flooding observed by 169.6ºC.  The melting point was thus between 167 and 169ºC.

**Henkin-McGill Cook-off Data**
About twenty-five 40±1 mg samples were tested to determine the small-scale critical temperature.  These samples had an average thickness of 0.071 cm.  The experimental data are shown in Figure 3 (go's and no-go's are denoted by open and filled symbols, respectively).  Little overlap was found between the go's and no-go's near the critical temperature.  The definition of the critical temperature is the temperature for the lowest go, ignoring that there may be some no-go's at higher temperatures.  Thus the critical temperature for this sample size of ANFO was determined to be 297ºC.  The positive tests were characterized by relatively weak events.

**SSCB Cook-off Data**
Two SSCB tests were run on approximately 25 g samples of ANFO in 1.6 cm diameter aluminum cylinders at temperatures above the melting temperature.  The results of the first SSCB test at 230ºC are shown in Figure 4.  The test temperature was reached in about 14 minutes.  After about 37 minutes, a rise in sample temperature is shown, followed by a temperature decrease.  Although this change in temperature appears relatively minor, visual monitoring of the test apparatus via a video camera showed that a short length of steel tubing connected to the vent fitting of the vessel had been ejected.  Smoke and particles escaped from the vent following this time, indicating that a cook-off had occurred.  The decrease in temperature was thought to be caused by ejection of a significant amount of the liquid ANFO, exposing the tip of the thermocouple and leading to lower temperature measurements.

The second SSCB test was run at a test temperature of 221ºC for about 180 minutes, followed by an additional 1600 minutes at 225ºC.  No chemical self-heating was observed.

The conclusion reached was that the critical temperature for this sample size of ANFO was between 221 and 230ºC, about 225ºC.

**1-Liter Cook-off Data**
One-liter isothermal cook-off tests were run[17] at 160, 163, 180, and 205ºC without observing thermal runaway.  However, visual monitoring of the tests showed that considerable gas evolution was occurring during the test, with resulting vigorous stirring of the molten ANFO at temperatures above 170ºC.  This prevented thermal runaway at the expected temperature (approximately 180-190ºC).  Because the primary interest was in solid ANFO and due to uncertainties in analyzing the data, additional 1-liter tests were not performed at higher temperatures.

**32-Liter Cook-off Data**
The first 32-liter cook-off test was performed using about 25 kg (55 pounds) of ANFO. In comparison with the smaller tests, the distance between the charge and the data acquisition was much greater in this case, about 210 meters (600 feet). This distance required electronic line drivers to send the thermocouple signals over long cables. The cook-off test was initiated at a wall temperature of 145°C. At about 4.1 days into this first large ANFO test, the apparatus suffered a near-hit from a lightening strike, and all of the control electronics were destroyed. When power was returned to the apparatus, shorted heater relays caused a fire. The ANFO burned slowly without incident.

The second 32-liter test setup was identical to the ill-fated first test. The initial wall temperature was set to 151°C. The ANFO, being a good thermal insulator, required about four days to reach the test temperature throughout the charge, as shown on the temperature profiles in Figure 5. No heat generation was observed during this period, so the wall temperature was increased to 158°C at a test time of 5.2 days. The charge was held under these conditions for about 2.5 days, during which the ANFO temperature gradually increased, but no self-heating was observed. The charge temperature again increased, this time to 162°C, just below the melting temperature of ANFO. The test was continued for another 2.1 days (from 7.7 to 9.8 days) without incident. The temperature was then increased to 165°C for about 0.8 day, and finally set to 175°C.

The final two days of the test are shown in Figure 6 on expanded scales. The mid-radius thermocouple signal was lost at about 9.2 days into the test (due to a thermocouple voltage-to-current module failure, again from lightening in the area). Upon increasing the wall temperature from 165 to 175°C, the center temperature signal began to increase and then showed an abrupt rapid increase when that temperature was 168°C. The ANFO temperature near the wall would have been slightly hotter. A rapid runaway reaction occurred which ignited the ANFO. Examination of the test vessel showed that about 90 percent of the ANFO burned, leaving a fused layer about 3-4 cm thick in the bottom of the vessel. The critical temperature for this test was concluded to be about 168±5°C.

## DATA ANALYSIS

**Thermal Conductivity of ANFO**
An accurate value for the thermal conductivity of ANFO was needed to predict and analyze cook-off data and to make safety calculations for storing large quantities of ANFO and AN prills. An experimental thermal conductivity value was obtained by analyzing the temperature profiles during the first 150 minutes of one of the 1-liter cook-off tests[20]. The ANFO did not begin to melt until after this time. The solid phase changes at 32, 84, and 125°C were evident in the temperature profiles (as was melting at later times). The endothermicity of these solid phase changes makes the thermal conductivity analysis uncertain, but we need an "engineering" value. By lumping the phase changes in with the heating processes, we obtained an effective thermal conductivity for practical use over this temperature range.

These calculations required values for the density and specific heat of ANFO. The density was measured as $0.85 \pm 0.01$ g/cm$^3$. A specific heat value from Urbanski[18] was used of 1.5 J/(g K), as measured for AN(III) at about 35-45°C. The value for the thermal conductivity of ANFO was varied until the calculated temperature profiles for the 1-liter test compared acceptably with the experimental data. Because of the phase changes, the fit was not as good as had been possible in previous work. The final value determined for the thermal conductivity of ANFO was 0.11 W/(m K), compared to that of high density AN of about 0.24 W/(m K).[23]

**Kinetic Analysis**
The three experimental critical temperatures from the Henkin, SSCB, and 32-liter cook-off tests were analyzed using the Frank-Kamenetskii formula to give reaction rate constants at each of the three temperatures. The following parameter values were used in the analysis:
• density of 1.65 g/cm$^3$ (measured) for Henkin and 0.85 g/cm$^3$ (measured) for SSCB and 32-liter
• thermal conductivity of 0.24 W/(m K) for Henkin and 0.11 W/(m K) for SSCB and 32-liter
• heat of reaction of 1260 J/g (300 cal/g)
• shape factors of 0.88 for Henkin, 2.5 for SSCB, and 2.7 for 32-liter

This analysis gave the following results:

## TABLE 1

| Test | Weight | Radius | Critical Temperature | Shape Factor | Rate Constant |
|------|--------|--------|----------------------|--------------|---------------|
| Henkin | 0.040 g | 0.035 cm | 297°C | 0.88 | $1.2 \times 10^{-2}$ s$^{-1}$ |
| SSCB | 25 g | 0.79 cm | 225°C | 2.5 | $2.5 \times 10^{-5}$ s$^{-1}$ |
| 32-liter | 22.7 kg | 20.5 cm | 168°C | 2.7 | $5.7 \times 10^{-8}$ s$^{-1}$ |

The expression fitting these points was k = $5.3 \times 10^{15}$ exp(-46.04/RT) s$^{-1}$ (Ea in kcal/mol) as shown in Figure 7. Also shown in Figure 7 are lines representing the ANMO data of Oxley, Kaushik, and Gilson and the FGAN data of Hainer over their respective temperature ranges. The agreement is excellent, even though the activation energies of the two earlier studies are lower than that of the current work.

**TOPAZ Simulations**
To test our ANFO kinetic and thermal parameters, we performed simulations of the SSCB and 32-liter cook-off tests using a PC version of the thermal code TOPAZ. TOPAZ-2D is a two-dimensional implicit finite element computer code for simulating chemical decomposition, heat transfer, and other problems. The code, which was originally written at

LLNL[19], can be used to solve steady-state and transient temperature fields for two-dimensional planar or axisymmetric geometries. Constant, isotropic properties for the explosive were used in this work. Chemical kinetics were modeled as a single, first-order reaction. A Turbo Pascal version[20] of TOPAZ-2D (hereafter referred to as TOPAZ) was used in this work and run on a 33 MHz 486 PC.

The model of the SSCB apparatus was developed using 14 points (nodes) defining 6 volume elements. The aluminum walls of the vessel, as well as the explosive, were included in the model. The outer wall temperature boundary condition included the finite time to reach the test temperature.

The TOPAZ model of the 32-liter apparatus included 77 nodes defining 60 volume elements. The glass walls of the vessel, as well as the air space between the ANFO and the heated vessel lid, were included in the model. The temperature boundary conditions were applied to the top, bottom, and sides of the vessel. The specific heating history of test #2 was used in the calculations.

The results of the two series of TOPAZ calculations are summarized below.

## TABLE 2

| Test | Temp. | Rate Constant | Time to Runaway Experiment | Calc. |
|------|-------|---------------|----------------------------|-------|
| SSCB | 230 | Standard | 40 min | 35 min |
| " | " | Std *0.50 | " | No runaway |
| " | " | Std *0.75 | " | 45 min |
| " | 220 | Standard | No runaway | No runaway |
| 32-liter | Test Profile | Standard | 10.77 days | 12.12 days |
| " | " | Std *0.50 | " | 14.47 days |
| " | " | Std * 2 | " | 11.16 days |
| " | " | Std * 5 | " | 7.07 days |

In simulating the SSCB test at 230°C, we initially used the ANFO decomposition rate constant determined in this work (denoted as "standard"). The TOPAZ calculation showed thermal runaway slightly faster than observed (35 minutes vs. 40 minutes observed). Although this is excellent agreement, a few additional runs were made to determine the sensitivity of the calculations to changes in the rate constant. When the rate constant was divided by 2, no runaway was computed. When it was reduced by 25 percent, runaway was calculated at 45 minutes. Thus the rate constant expression is probably accurate within about 10 percent at

230°C.

At 220°C, where no SSCB runaway was experimentally observed, the standard rate constant expression gave no computed runaway.

In the TOPAZ simulations of the 32-liter cook-off tests, the standard rate constant gave runaway slightly slower than was observed.  Multiplying and dividing the rate constant by 2 and then multiplying by 5 gave results that indicate that the rate constant expression may be slightly low, by about a factor of 2, in the temperature region of 150-165°C.  This uncertainty is about the same magnitude as the square points which represent the data in Figure 7.

**Applications to Large Charges**
With reason to think that extrapolation of the ANFO thermal stability model calculations on large storage quantities was reasonably valid, some calculations on field applications were performed.

The variation of critical temperatures for ANFO cylinders and spheres with increasing diameters was calculated using the simple F-K formula and the input parameters discussed above.  These critical temperature results are shown vs. charge weight on a logarithmic scale in Figure 8.  The linear relationship shown in this figure indicates that the critical temperatures decrease by about 10°C for every ten-fold increase in the mass of ANFO.  As a point of reference, a 55-gallon drum has a radius of about 28 cm and would weigh about 175 kg (385 pounds) when filled with ANFO.  The critical temperature for such a drum would be 158°C.  A 1-ton cylinder with diameter equal to length would have a diameter of 55 cm and a critical temperature of 147°C.

Specific calculations were performed for hemispheres of 2,400 and 4,800 tons of ANFO.  These charges would have diameters of 2140 and 2700 cm, respectively, at a density of 0.85 g/cm$^3$.  F-K calculations were performed using these diameters, the model parameters given above, and a shape factor of 3.33 (sphere), ignoring that the charges were only half spheres.  This assumes that the interface between the ANFO and the ground is approximately adiabatic.  Critical temperatures are given below for the standard rate constant, and for the rate constant multiplied and divided by a factor of two.  Since the uncertainty in the rate constant is thought to be less than this factor, a conservative range of critical temperatures were calculated to include this and other uncertainties.

# TABLE 3

| ANFO Charge Size | Critical Temperature | | |
| --- | --- | --- | --- |
| | Std. / 2 | Standard | Std. x 2 |
| 2,400 tons | 112°C | 107°C | 103°C |
| 4,800 tons | 109°C | 104°C | 100°C |

Thus the final F-K results are 107±4°C and 104±4°C for the 2,400 and 4,800-ton charge sizes.

**TOPAZ Calculations**
A TOPAZ model of a 2,400-ton hemisphere of ANFO (diameter = 2140 cm) was created using 42 nodal points defining 31 volume elements. Because of the large size of the charge, the thermal effects of the container were ignored.

The first calculations were made using a constant elevated temperature boundary condition at the outside surface of the charge. Runs were made with this temperature set to 110, 125, and 140°C, with the initial ANFO temperature at 35°C. The calculations were run to simulate a 30-day period under these conditions. No thermal runaway occurred in these calculations; in fact, the ANFO is such a good thermal insulator that the temperature increase was limited to the material near the surface of the container. Another simulation was run with the surface temperature at 165°C, well above the critical temperature, and the initial ANFO temperature at 80°C. Although the temperature of the material near the surface exceeded 100°C, no significant heat generation or runaway was seen in the calculation.

We concluded that heating in this manner (i.e., by conduction from the outside surface of the hemisphere) is not likely to create a runaway situation in any credible scenario.

**CONCLUSIONS**

Overall, the work reported here showed ANFO to be a highly thermally stable energetic material, suitable for use in large conventional explosive charges even with high ambient temperatures. The data measured in this work allow quantitative predictions of minimum thermal runaway conditions for ANFO charges of various sizes and for various initial conditions. If the initial temperature of ANFO loaded into a container such as a hemisphere of 2,400 tons (20 meters (70 feet) in diameter) is near ambient, our model indicates that no credible external heating is likely to bring the material to a runaway condition. The main remaining hazards are from a large fire at the surface or inside the ANFO or in some other nearby fuel, or from accidental detonation of some other explosive, such as a high explosive booster charge, near the ANFO.

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# Figure 1. Arrhenius graph of literature data on AN/fuel mixtures.
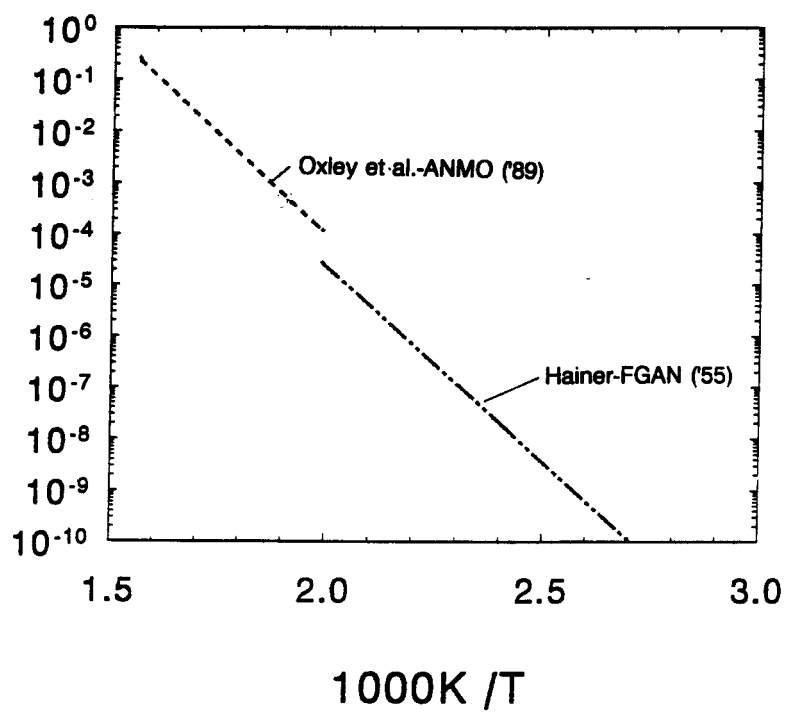


Figure 1. Arrhenius graph of literature data on AN/fuel mixtures.

# Figure 2. Arrhenius graph of literature data on AN
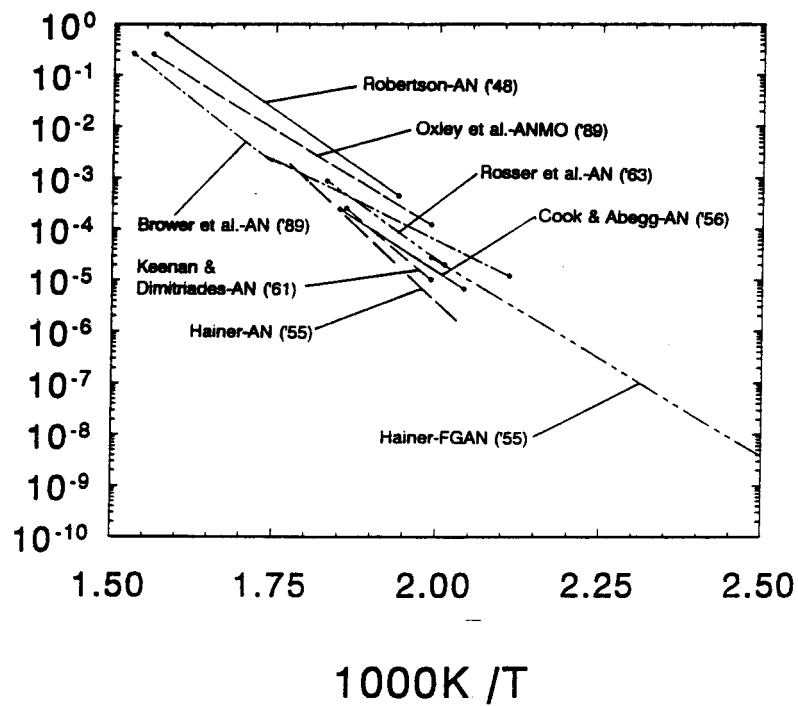


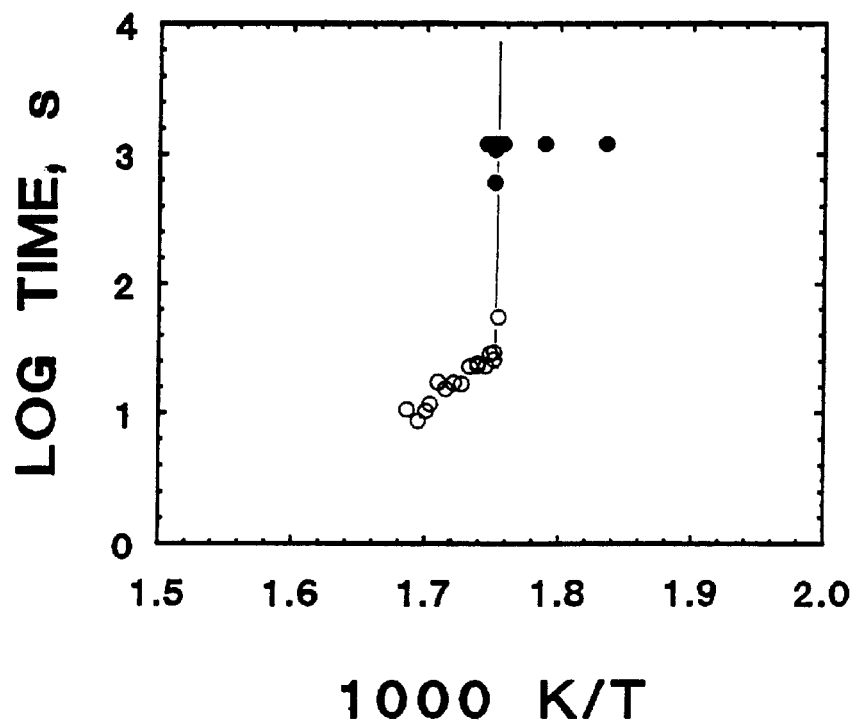Figure 2. Arrhenius graph of literature data on AN

**Figure 3. Henkin-McGill data for 40 mg cook-off tests on commercial ANFO. The filled symbols represent no-go results and the open symbols represent go's. The critical temperature was found to be 297°C.**



Figure 3.    Henkin-McGill data for 40 mg cook-off tests on commercial ANFO. The filled symbols represent no-go results and the open symbols represent go's. The critical temperature was found to be 297°C.

# Figure 4. SSCB cook-off test #1 for ANFO. An event occurred at about 38 minutes at 230°C.
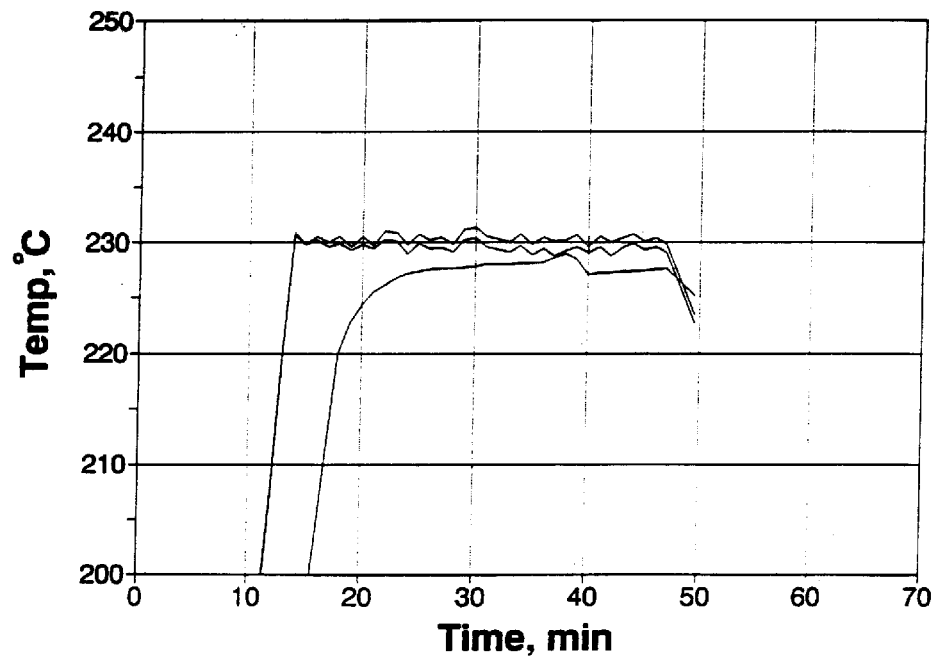


Figure 4. SSCB cook-off test #1 for ANFO. An event occurred at about 38 minutes at 230°C.

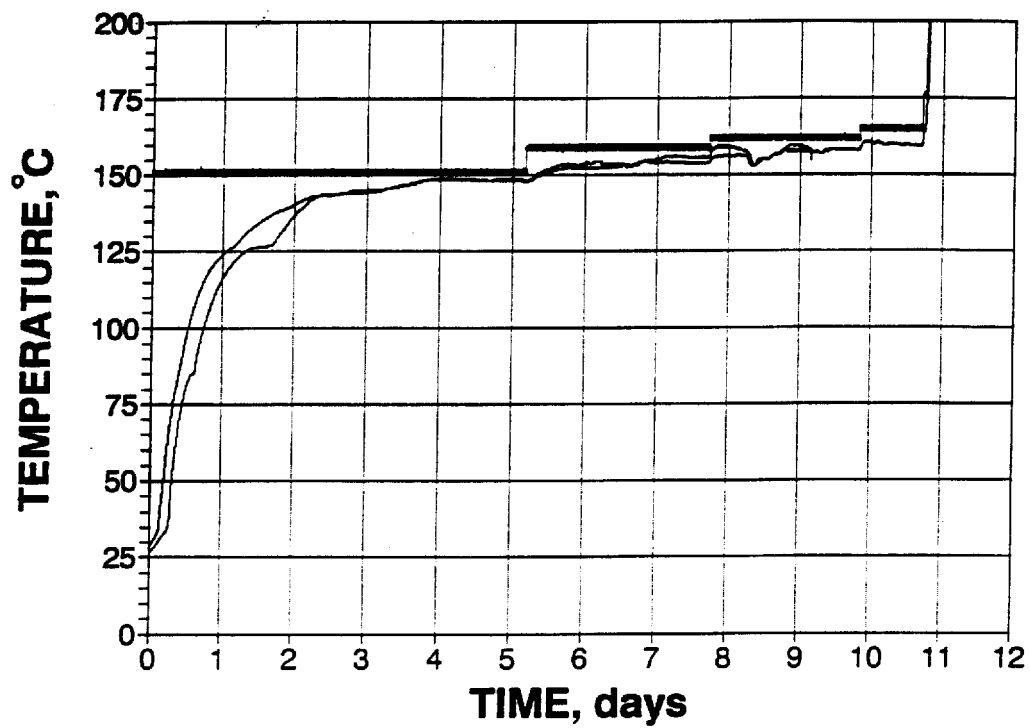# Figure 5.  Temperature Data for 32-Liter Cook-off Test #2.



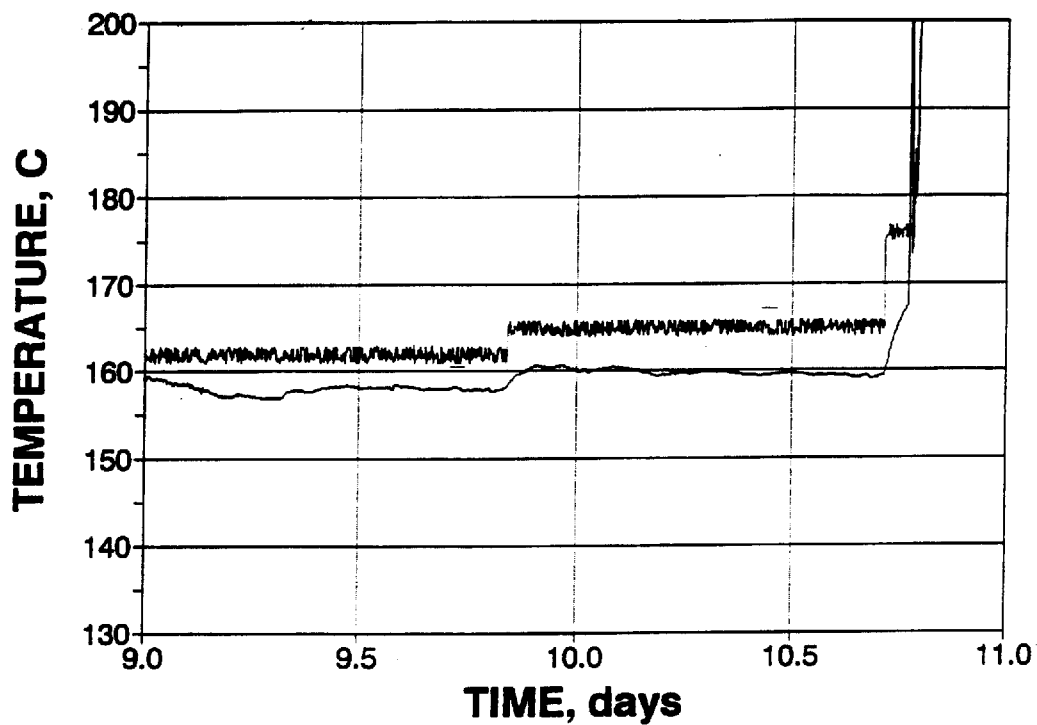Figure 5.  Temperature Data for 32-Liter Cook-off Test #2.

**Figure 6. 32-Liter Cook-off Data on Expanded Scale. The sample exhibited rapid self-heating soon after the temperature was increased at 10.75 dyas. The ANFO burned.**



Figure 6.  32-Liter Cook-off Data on Expanded Scale. The sample exhibited rapid self-heating soon after the temperature was increased at 10.75 dyas. The ANFO burned.
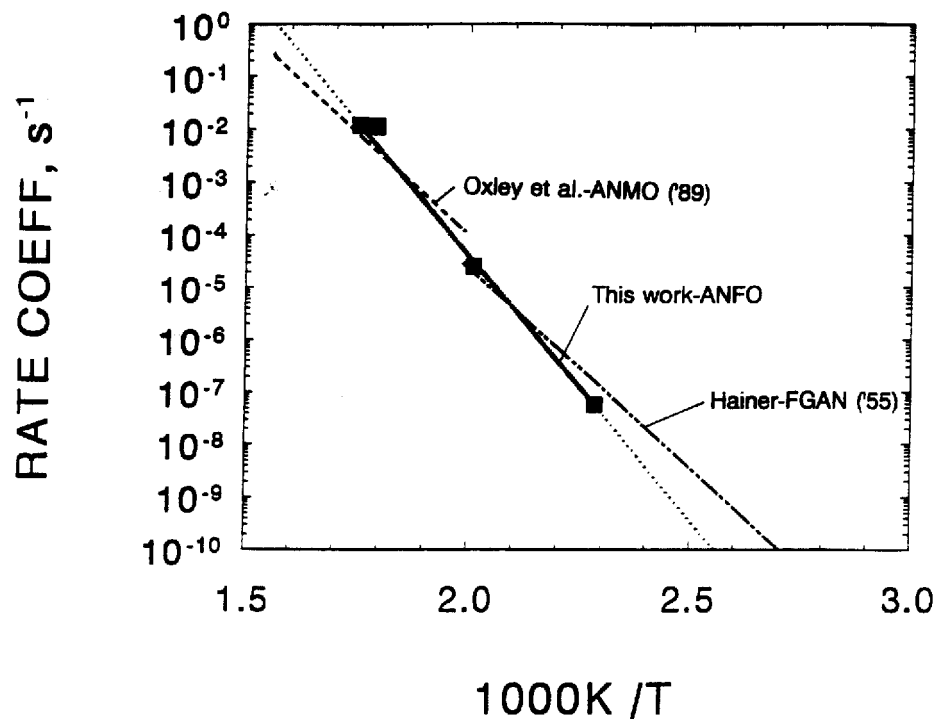
**Figure 7. Arrhenius Graph of ANFO Decomposition Data. The filled points are the experimental data from this work. The expressions of Oxley et al. and of Hainer are shown for comparison.**



Figure 7.   Arrhenius Graph of ANFO Decomposition Data.  The filled points are the experimental data from this work.  The expressions of Oxley et al. and of Hainer are shown for comparison.

# Figure 8. Calculated critical temperatures for large ANFO spheres. Predictionsmade using the F-K formula and input parameters discussed in the text.
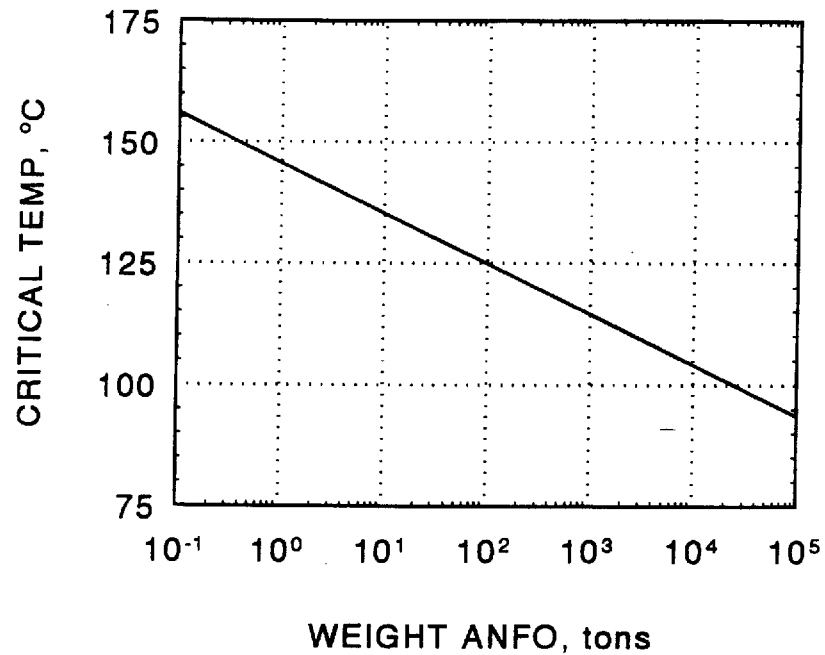


Figure 8.   Calculated critical temperatures for large ANFO spheres.  Predictions made using the F-K formula and input parameters discussed in the text.